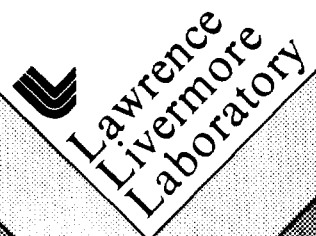


Materials Considerations for the Coupling  
of Thermochemical Hydrogen Cycles  
to Tandem Mirror Reactors

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# MATERIALS CONSIDERATIONS FOR THE COUPLING OF THERMOCHEMICAL HYDROGEN CYCLES TO TANDEM MIRROR REACTORS\*

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## Abstract

Candidate materials are discussed and initial choices made for the critical elements in a liquid Li-Na Cauldron Tandem Mirror blanket and the General Atomic Sulfur-Iodine Cycle for thermochemical hydrogen production. V and Ti alloys provide low neutron activation, good radiation damage resistance, and good chemical compatibility for the Cauldron design. Aluminide coated In-800H and siliconized SiC are materials choices for heat exchanger components in the thermochemical cycle interface.

## Introduction

This paper describes some of the initial materials considerations for utilizing a Tandem Mirror Reactor (TMR) fusion heat source for the thermochemical production of hydrogen from water. The rationale for future hydrogen needs in this country, and an overview of the overall study have been given previously by Werner,<sup>1</sup> and a number of the chemical engineering considerations in interfacing the TMR heat source to a thermochemical hydrogen cycle have been discussed by Galloway.<sup>2,3</sup>

Briefly, the main TMR blanket design concepts under consideration in this study are (1) a binary liquid Li-Na Cauldron design where heat is removed by the preferential boiling of Na, and (2) a moving bed design that uses  $\text{Li}_2\text{O}$  microspheres of  $\sim 0.5$  mm diameter. The main thrust at this time is to investigate the problems of coupling the Li-Na Cauldron to the General Atomic (G.A.) Sulfur-Iodine Thermochemical Cycle and our materials considerations here will refer only to this combination. Details of the Cauldron design have been given by Werner<sup>1</sup> and the interfacing with the G.A. Cycle by Galloway.<sup>2</sup>

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The cauldron concept-housing a hot fluid in a cool container

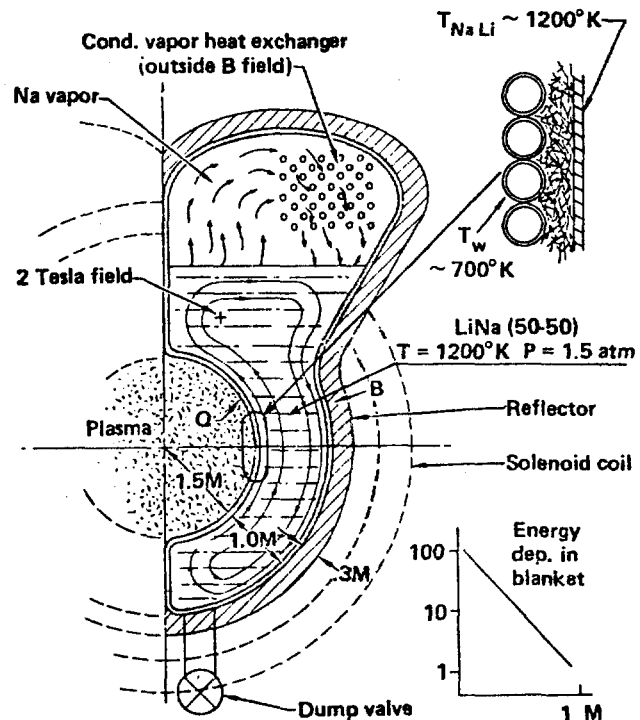


Fig. 1. Schematic view of the Li-Na Cauldron design.

In the Cauldron design, a number ( $\sim 150$ ) of modular blanket units are installed along the length of the central cylindrical section of the TMR (see Fig. 1). Heat deposited by neutron moderation in the Li-Na pool is transferred by microconvective processes to the pool surface where Na, due to its high vapor pressure ( $\sim 1.5$  atm at 1200K) boils off and transfers its latent

heat of vaporization to a condensing vapor heat exchanger. Na then returns to the pool along the side furthest from the plasma, and because of its reduced temperature and high density moves rapidly toward the bottom of the pool and re-enters the convective boiling process. Structural strength for the Cauldron module is provided by a cooled outer structural wall constructed of tubular cooling channels operated at  $\sim 700\text{K}$ . An inner wall at the full temperature ( $\sim 1200\text{K}$ ) of the liquid metal pool provides for its containment, and in-between the structural wall and the inner wall, we use a fibrous metal insulator to limit the outward heat flow.

Process heat from the blanket module for the thermochemical cycle is provided primarily by the condensing vapor heat exchanger at  $\sim 1200\text{K}$ . Additional heat at  $\sim 700\text{K}$  is also supplied by the cooled structural wall. Materials problems associated with the heat exchangers and transport piping involved in interfacing the Cauldron heat source to the thermochemical cycle will be discussed in this report.

A brief description is given next of thermochemical cycles in general and of the G.A. Cycle in particular in order to indicate the key areas in which heat input is required and where the main materials problems exist.

A thermochemical cycle for hydrogen production is a process in which water is used as a feedstock along with a non-fossil high temperature heat source to produce  $\text{H}_2$  and  $\text{O}_2$  as product gases. The water splitting process is accomplished through a closed loop sequence of chemical reaction steps in which the chemical reagents are continuously recycled and reused in the process with essentially no loss of material. Practical thermochemical cycles, as currently envisioned, require input temperatures of  $\sim 1200\text{K}$  for the highest temperature chemical step, and operate at a thermal efficiency of  $\sim 45\%$ . Here, the thermal efficiency is defined as the higher heating value of the  $\text{H}_2$  produced,  $285.9 \text{ kJ/g mol H}_2$  (combustion enthalpy of the  $\text{H}_2$  to give liquid water at  $298.15\text{K}$ ) compared with the thermal heat delivered by the heat source.

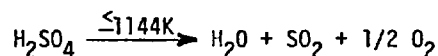
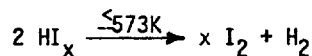
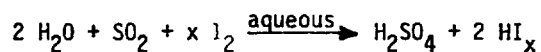
Currently, there are some thirty thermochemical cycles worldwide that are under various stages of investigation and development. Energy sources that are being considered for these cycles fall into three categories: (1) high temperature gas cooled reactors providing a maximum temperature of  $1200\text{K}$ , (2) solar central receivers providing a maximum temperature somewhere in the  $1200\text{-}2000\text{K}$  range, and (3) magnetic fusion reactors anticipated to provide a maximum temperature in the  $1200\text{-}2000\text{K}$  range. Selection of an actual maximum operating temperature depends upon the process needs of the thermochemical cycle as well as an overall system

design. Cycle efficiency, system economics, and materials needs are all important considerations. Electrical energy for process equipment is required in addition to high temperature process heat for operation of thermochemical hydrogen plants.

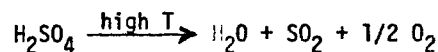
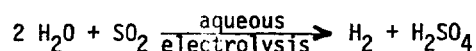
Of the cycles under study, only three cycles have thus far been developed to the stage where closed loop table-top models have been built and tested in the laboratory, and these are the cycles that we are considering for magnetic fusion applications. They are illustrated in terms of their principal chemical steps and reaction temperatures in Figure 2. The main effort on the development of the Sulfur-Iodine Cycle is underway at the General Atomic Company,<sup>4-6</sup> for the Sulfur Cycle at the Westinghouse Electric Corporation,<sup>7-9</sup> and for the Sulfur-Bromine Cycle at the Commission of European Communities Joint Research Centre-Ispra Establishment.<sup>10-12</sup>

Figure 2. Thermochemical cycles whose chemistry and closed loop operation have been verified in the laboratory

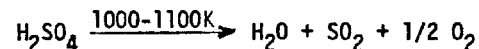
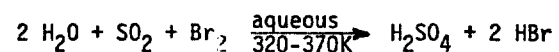
#### Sulfur-Iodine Cycle



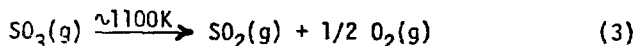
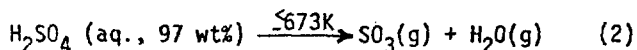
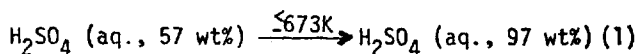
#### Sulfur Cycle (part electrochemical)



#### Sulfur-Bromine Cycle (part electrochemical)



In the G.A. Cycle, the third major reaction step is the one that requires most of the process heat, and this step needs to be broken down into further detail to better illustrate the heat requirements. Thus, the main endothermic reactions that contribute to the third major reaction step in the G.A. Cycle are as follows:



In reaction (1), aqueous  $\text{H}_2\text{SO}_4$  that is produced near room temperature at 57 wt% is concentrated to about 97 wt% by evaporating off excess water to form the azeotropic boiling composition. The azeotrope is then boiled according to reaction (2) at 673K and 10 atm pressure. This sequence of  $\text{H}_2\text{SO}_4$  concentration and boiling of the azeotrope is one of the primary heat consuming steps of the cycle. Subsequent to boiling the  $\text{H}_2\text{SO}_4$ , the gaseous  $\text{SO}_3/\text{H}_2\text{O}$  mixture is heated to  $\sim 1100\text{K}$  where most of the  $\text{SO}_3$  decomposes to form  $\text{SO}_2$  and  $\text{O}_2$ . This then constitutes the second major heat consuming step in the cycle and also the step that requires the highest temperature input. Significant amounts of high temperature heat are also needed for shaft and electrical power in the cycle. Our main concerns here will be to identify materials for the  $\text{H}_2\text{SO}_4$  boiler and the  $\text{SO}_3$  decomposer heat exchangers. These processes both present highly corrosive conditions for heat exchanger materials. Hence, corrosion resistance is one of our main considerations in selection of heat exchanger materials.

#### Blanket Materials

The most important elements of the Cauldron design from a materials standpoint are the following:

- First wall portion of the structural wall
- "Feltmetal" insulator\*\*
- Cauldron wall
- Condensing vapor heat exchanger
- Tritium permeation membranes

Criteria for the selection of materials for these elements and the initial selections that have been made will be described in turn.

#### First Wall (Structural Wall)

The major considerations for selection of materials for the first wall are neutron activation and radiation damage effects. Hence, our current best choices for first wall materials

\*\*Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Dept. of Energy to the exclusion of others that may be suitable.

are V-10% Ti and V-20% Ti, since both V and Ti show minimal neutron activation, and the V-10% Ti and V-20% Ti alloys suppress He gas bubble formation as contrasted with other V alloys.<sup>13</sup> We also anticipate that tritium impact should not cause problems of localized tritium buildup in the first wall, since tritium should permeate very rapidly through V and its alloys. Recent work by Hisamatsu and Kanno has shown that hydrogen permeation rates are actually about ten times higher in V than in Nb at  $\sim 700\text{K}$ , and second only to Pd or Pd-Ag alloys.<sup>14</sup>

In other considerations regarding the use of V for the first wall, we need to evaluate corrosion problems, fabrication, and material cost. Three coolants have been considered for the first wall, i.e., liquid Na, He, and organic liquids (polyphenyls) and the corrosion characteristics vary according to the coolant. According to a compilation by Cowles and Pasternak,<sup>15</sup> V shows good resistance to corrosion by liquid Li at  $\sim 1100\text{K}$ , and because of the similarity in corrosion behavior by alkali metals in general, and the lower temperatures required here ( $\sim 700\text{K}$ ), we anticipate good resistance to liquid Na or K as well. Helium should not present any corrosion problems. Nor do we anticipate corrosion with the liquid polyphenyls, but radiation damage can lead to carbon deposition in the tube passages unless the polyphenyls are continuously processed and purified to remove decomposition products that result from radiation damage.

The technology of producing V sheet or tubing, and fabrication by electron beam welding, is similar to that for Nb and Ta and presents no problems as long as interstitial O, N, and H are kept at low levels.<sup>16</sup> In particular, O and N contents should not exceed 2000 ppm by weight otherwise V will become brittle. Even this problem can be alleviated by alloying the V with Y.<sup>17</sup>

Historically, the demand for pure V has been relatively small, and as a result the production has been limited and the cost high. V resources, both in this country and in the world, are extremely large, but V does not normally occur as a pure ore and must be recovered as a by-product of other metal manufacture - it is especially recovered from titaniferous magnetite ores.<sup>18</sup> Currently, the principal use of V is as an additive to steels, at a use rate of about 5000 tons/year in the U.S. The current cost of pure V is \$550-620/kg in small quantities, and less than \$440/kg in large quantities. We anticipate that increased usage of V will lead to major reductions in its cost. Using a cost of \$440/kg gives an estimated raw material cost for V in the first wall ( $\sim 25 \text{ Mg}$  required) of about eleven million dollars.

We are considering beta-Ti alloys as a back-up material for the first wall. A clear judgment on this is yet premature because of the lack of sufficient information on the radiation damage behavior of beta-Ti alloys. It is encouraging that the tritium (hydrogen) diffusivity in beta-Ti alloys is substantially higher than in alpha-Ti alloys,<sup>19</sup> so that tritium concentration buildup within the material with subsequent degradation of physical/mechanical properties should be much less a problem in beta-Ti than in alpha-Ti. The beta structure can be stabilized by alloying additions of V, Cr, Fe, Mo, or Al.

A much broader range of conventional low-cost alloys (e.g., Fe-Ni based alloys) can be used for the structural wall outside of the first wall region, where neutron activation and radiation damage effects are greatly reduced.

#### Feltmetal Insulator

Requirements for the insulator between the outer structural wall and the Cauldron wall are that it have good resistance to neutron activation and radiation damage in the first wall region, that it provide the necessary thermal insulation, that it have good compressive strength to support the Cauldron wall, that it have low shear strength to provide for differential expansion of the inner and outer walls, and that it provide a porous channel for removal of tritium that permeates through the walls. The commercial fibrous metal insulator called "Feltmetal" seems to essentially meet all of these requirements for material with a bulk density of ~40% of theoretical. Further, it should be possible to fabricate Feltmetal from any of the ductile metals. From the standpoint of neutron activation, the best candidates are V and Ti, and because of the lower cost of Ti, it is the preferred material. Either a fully or partially beta-stabilized alloy should be used to maintain material integrity over the full temperature range (The alpha-beta transformation in Ti occurs at 1155K). The alloys Ti-13V-11Cr-3Al, Ti-2.5Al-16V, and Ti-7Al-4Mo are our current selections based on existing commercial alloys. However, creep may be a problem with these alloys at the upper end of the temperature range where the Feltmetal is in contact with the Cauldron wall. This can be alleviated by developing new Ti alloys specially designed for high temperature strength, or by using a layered or graded structure in the Feltmetal varying from a Nb alloy next to the Cauldron wall to a Ti alloy next to the structural wall.

#### Cauldron Wall

For the Cauldron wall, the main materials considerations are: neutron activation and radiation damage in the region near the plasma, corrosion and long-term creep strength for the

entire wall region, and the existence of a fabrication technology for the Cauldron structure. As with the Feltmetal, we have selected the beta-Ti alloys for the Cauldron wall to minimize neutron activation and radiation damage, and to minimize the use of the more costly V.

Pure Ti metal shows good corrosion resistance to liquid Li at 1000-1200K,<sup>20</sup> and similar behavior can be expected with liquid Na or K. Alloying additions of V, Cr, Fe, or Mo to stabilize beta-Ti should not effect the corrosion resistance, since these elements also have excellent resistance to corrosion by alkali metals. Al, by itself, is reactive with the alkali metals, but when alloyed in low concentrations in Ti, can be expected to have a major reduction in reactivity because of a lowering of its chemical activity. Thus, we believe that a few percent Al is acceptable as an alloying additive.

It is difficult to fully assess the problems of long-term creep in beta-Ti alloys at ~1200K at this time. Although the stress levels on the Cauldron are quite low, there is no experimental creep data on beta-Ti alloys at the temperatures of interest. Short-term yield strengths generally remain quite high for Ti alloys at temperatures in the vicinity of 1200K, e.g., for MST 881 a Ti-8Al-8Zr-1(Nb+Ta) alloy,<sup>21</sup> the short-term tensile yield strength (0.2% deformation) is 33,200 psi ( $2.3 \times 10^8$  Pa) at 1200K.

Fabrication and welding of both alpha- and beta-Ti alloys into large complex structural units using a electron beam welding techniques has been well-established as a technology by the aerospace industries.<sup>22</sup>

#### Condensing Vapor Heat Exchanger

The condensing Na (or K) vapor heat exchanger at a top of the cauldron dome can be accommodated in two ways: (1) using heat exchanger tubes containing liquid Na or K or gaseous He, or (2) using heat pipes with Na as the working fluid. If heat pipes are used, a secondary loop would still be required with circulating Na, K, or He to carry the heat to the thermochemical plant. A high thermal conductivity, good corrosion resistance, creep resistance, and ease of fabrication are important considerations for the condensing vapor heat exchanger. Molybdenum alloys, particularly TZM, have a distinct advantage in heat pipe and heat exchanger applications where high thermal conductivities are needed to minimize temperature drops. Molybdenum alloys also have high strengths and outstanding resistance to corrosion by liquid alkali metals.<sup>20</sup> Small-scale (up to ~3 cm in dia.) welding of molybdenum heat pipes and laboratory test capsules is well-established, but large component welds are not currently part

of our technology. We have therefore selected TZM as the best candidate for heat pipe or heat exchanger applications in the Cauldron dome.

We are also considering Nb alloys, Ta alloys, and In-800 (or In-800H) as possible alternate materials. The Nb and Ta alloys have excellent corrosion resistance to the alkali metals, while that for In-800 may be marginal. The common Nb alloys, Nb-1Zr and Nb-10Ti-10Mo have markedly lower creep strengths than TZM. D-43, a developmental grade alloy of composition Nb-9W-1Zr, has a creep strength comparable to TZM,<sup>23</sup> and should be considered as a viable alternative if it goes into commercial production. TZM still has the advantage of a higher thermal conductivity. The Ta alloys T-111 (Ta-8W-2Hf) and T-222 (Ta-10W-2.5Hf) also have creep strengths comparable to TZM, but again are only developmental alloys. Fabrication of the Nb and Ta alloys should present no problems. An area of concern however is the presence of Zr and Hf in these materials, since they have an affinity for hydrogen that may lead to a holdup of tritium in the alloys. In-800 and In-800H are attractive because of their low cost, ease of fabrication, and good creep resistance for an Fe-Ni based alloy, although much lower than for TZM. Dropping the use temperature to 1100K for In-800 greatly improves its creep strength and corrosion resistance properties. Thus, creep strength for 1% creep in 100,000 h becomes 2000 psi + 50% ( $1.4 \times 10^7$  Pa),<sup>24</sup> and corrosion in liquid Na, as determined by Nevzorov for an alloy with a composition similar to In-800,<sup>25</sup> was found to be  $7.5 \times 10^{-3}$  mg/cm<sup>2</sup>-h in a 300 h run. Conservatively assuming a linear corrosion rate, gives 82  $\mu$ m corrosion in one year, while assuming a parabolic (diffusion-controlled) rate, gives 1.5  $\mu$ m corrosion in one year. In either case, good corrosion resistance is indicated for In-800 at 1100K.

#### Tritium Permeation Membranes

Tritium released from the boiling Li-Na pool will need to be recovered through several paths. A portion can be recovered from the Feltmetal channel, a portion will pass into the heat exchange loop or heat pipes, and a portion can be intentionally removed through permeation membranes in the vapor dome. Without pursuing design specifics, it should be clear that materials that have a high permeation rate for tritium and that will withstand corrosion by the liquid metal environment, will be needed for tritium recovery in this system.

V alloys are the best choice for permeation membranes from the standpoint of tritium permeation rates.<sup>14</sup> Va also shows good resistance to corrosion by liquid Li at temperatures of  $\sim$ 1100K,<sup>15</sup> and we anticipate that it will be resistant to liquid Na and K as well. Other

candidate materials are Nb and beta-Ti alloys. Nb alloys are to be preferred where high strength and low creep rates are required.

#### Process Chemistry Materials

The critical materials problems associated with interfacing the cauldron blanket design with the General Atomic Sulfur-Iodine Cycle involve the following design elements:

- Transport piping
- Heat exchanger - SO<sub>3</sub> decomposer
- Heat exchanger - H<sub>2</sub>SO<sub>4</sub> boiler

The transport piping deals with transport of heat from the Cauldron to the thermochemical process - i.e., mainly to the SO<sub>3</sub> decomposer and the H<sub>2</sub>SO<sub>4</sub> boiler sections. The heat exchangers for the SO<sub>3</sub> decomposer and H<sub>2</sub>SO<sub>4</sub> boiler present the most serious design and materials problems in the thermochemical plant, and so we have chosen to emphasize them in our initial study here. Although the materials problems are discussed in terms of the General Atomic Cycle, the problems are common to the Ispra and Westinghouse Cycles as well, because of the commonality of the H<sub>2</sub>SO<sub>4</sub> handling steps. Each of the design elements indicated above will be described in turn in the sections below.

#### Transport Piping

The main materials considerations for the transport piping are corrosion resistance, good creep strength, low cost, and ease of fabrication. We envision the transport piping to be surrounded by a porous insulating blanket and a jacket, with a sweep gas passing through the insulating layer to remove any residual tritium. The heat transport fluid in the main pipe would be either liquid Na, liquid K, or high pressure He at temperatures of about 1100-1150K.

Corrosion considerations are similar for using liquid Na or K as the heat transport fluid, and taking into account the materials considerations above, we find that In-800 (or In-800H) provides the best piping material. As mentioned earlier in this paper, corrosion rates for In-800 in liquid Na are very low at  $\sim$ 1100K, and we can expect similar behavior in liquid K.

With high pressure He, corrosion is no longer a problem, and from a consideration of creep strength, cost, and fabrication issues, In-617, In-625, and In-800 (or In-800H) provide the best alternatives. Stress rupture and creep properties for In-625 and In-800 are comparable,<sup>26</sup> while although creep strength data are not available for In-617, it shows 1000 hour

stress rupture strengths that are 3 times higher<sup>26</sup> than for the other two alloys. Thus, the data for In-625 and In-800 indicate a creep strength for 1% creep in 100,000 hours of  $2000 \pm 50\%$  psi ( $1.4 \times 10^7$  Pa) at 1100K and  $1200 \pm 30\%$  psi ( $8.2 \times 10^6$  Pa) at 1150K. We estimate the corresponding values for In-617 to be  $6000 \pm 50\%$  psi ( $4.1 \times 10^7$  Pa) at 1100K and  $3600 \pm 30\%$  psi ( $2.4 \times 10^7$  Pa) at 1150 K, based on the argument that the creep strengths scale as a fraction of the long term creep rupture data similar to In-625 and In-800.

#### Heat Exchanger - SO<sub>3</sub> Decomposer

The highest temperature heat requirement in the General Atomic Sulfur-Iodine Cycle is for the SO<sub>3</sub> decomposer, which operates at a temperature of ~1100K. Process heat would be delivered either by liquid Na, liquid K, or high pressure He to heat exchanger tubes 2 cm in diameter and 2-3 mm wall thickness. Materials considerations on the heat delivery side of the heat exchanger are similar to those for the transport piping, while on the chemical process side, corrosion by the decomposing SO<sub>3</sub> gas is of major concern.

Corrosion tests on a number of heat exchanger alloys for the H<sub>2</sub>SO<sub>4</sub> vapor decomposer have been carried out at Ispra and at the General Atomic Company at temperatures in the 773-1173K range. Their latest results<sup>27</sup> indicate that as bare uncoated alloys, In-800H and In-625 provide the best materials with anticipated lifetimes of a few years. A substantial gain in lifetime can be achieved by using an aluminide-coated In-800H on the surface exposed to the decomposing SO<sub>3</sub> gas. This gives an unusually stable coating-substrate combination that stabilizes in coating thickness and weight change after an exposure of 200-300 hours to the gaseous H<sub>2</sub>SO<sub>4</sub> products.<sup>9</sup> Corrosion protection is apparently afforded by an Al<sub>2</sub>O<sub>3</sub> film, and imperfections in the coating are self-healing. The useful life of aluminide-coated In-800H for this application is believed to be of the order of 20 years.

In view of the experience with aluminide-coated In-800H in the presence of the decomposing SO<sub>3</sub> gas, and in view of data by Nevzorov<sup>25</sup> that indicates good corrosion resistance to liquid Na for an alloy similar in composition to In-800H, we select In-800H as the material of choice for the heat exchanger tubes. Unfortunately, the allowance in wall thickness due to corrosion by liquid Na or K cannot be established with certainty for a 20 y life. Based on the 300 h test data of Nevzorov, and using a linear corrosion rate with time, gives 1.6 mm of corrosion in 20 y. For a parabolic corrosion rate with time (a solid-state diffusion controlled process), the corrosion amounts to 7  $\mu$ m in 20 y. We believe that the diffusion

controlled process is probably the one that prevails, i.e., the diffusion of Ni (the most soluble constituent) into the liquid Na stream. Use of a 0.5 mm thick steel clad applied to the heat exchanger walls that are exposed to liquid Na or K, provides us with an alternative approach to avoid corrosive attack. A clad with Fe-2.25 Cr-1Mo should give the required corrosion resistance as well as avoid hydrogen embrittlement problems due to traces of hydrogen in the liquid alkalis.

Use of He as the heat transport fluid avoids the corrosion problems on the heat input side of the heat exchanger, but we are still committed to the use of In-800H with an aluminized coating on the SO<sub>3</sub> side, since corrosion protection there remains a requirement.

#### Heat Exchanger - H<sub>2</sub>SO<sub>4</sub> Boiler

The most critical corrosion problem in the General Atomic Sulfur-Iodine Cycle is corrosion of the heat exchanger used to boil a concentrated azeotropic solution of H<sub>2</sub>SO<sub>4</sub>. This boiling step is carried out at ~673K and ~10 atm pressure using the azeotropic composition of H<sub>2</sub>O-H<sub>2</sub>SO<sub>4</sub> that occurs at 97 wt% H<sub>2</sub>SO<sub>4</sub>. The high temperature and pressure are required to minimize equipment size and gas pumping power. Under these boiling conditions, the liquid phase H<sub>2</sub>SO<sub>4</sub> is highly corrosive to all known metallic heat exchanger materials (except for the Pt group metals and Au, which are too expensive for consideration).

A number of materials have been tested in hot concentrated H<sub>2</sub>SO<sub>4</sub> at 633-693K in recent years at the Lawrence Livermore National Laboratory<sup>28,29</sup> and at Westinghouse<sup>9</sup> to identify materials that can be used for the H<sub>2</sub>SO<sub>4</sub> boiler. The top candidate materials from the standpoint of corrosion resistance and heat exchanger design are the following:

- Siliconized SiC
- "CrSi<sub>2</sub>" coated In-800
- Durichlor-51 (Fe-14% Si-4% Cr)

All of these materials depend upon the development of an SiO<sub>2</sub> scale on the surface to provide protection against corrosion by H<sub>2</sub>SO<sub>4</sub>.

SiC currently presents the best prospect as a heat exchanger material. Siliconized SiC (a two phase composition consisting of a mixture of SiC and Si) is produced at the Norton<sup>30</sup> and Carborundum<sup>31</sup> companies and is especially suited for this type of application. This type of material, which contains about a 10-15 wt% excess of silicon metal, is impervious to gases, has a high thermal conductivity, high strength, good thermal shock resistance, and can be



fabricated in complex shapes and bonded together to form heat exchanger assemblies.<sup>30</sup> Corrosion testing of SiC for 1121 h and Si for 592 h in 97 wt% H<sub>2</sub>SO<sub>4</sub> at 673K at the Lawrence Livermore National Laboratory showed no evidence of corrosion,<sup>28</sup> thus confirming the corrosion resistance of both SiC and Si for this application.

Specimens of In-800 coated with chromium silicide of nominal composition CrSi<sub>2</sub> were tested for corrosion for 240 h at 673K in 97 wt% H<sub>2</sub>SO<sub>4</sub> at the Lawrence Livermore National Laboratory<sup>29</sup> and found to show a very low rate of corrosion (extrapolates to a weight loss rate of 15 mg/cm<sup>2</sup>-y). The coatings were about 120 μm thick, uniform in thickness, well-bonded to the substrate, and without evidence of fractures. The coatings were prepared by Dr. Charles M. Packer of Lockheed Missiles and Space Company of Palo Alto, California, using a slurry coat and rapid melt technique. Although the above results are preliminary in nature, they are encouraging in that a conventional heat exchanger material such as In-800 can be protected against corrosion by a coating process.

Durichlor-51 is a commercial high silicon cast iron material that is yet another candidate as a heat exchanger or container material. It is basically an intermetallic compound with a composition of approximately Fe<sub>3</sub>Si, and as such presents the disadvantages common to most intermetallics of poor ductility, low tensile strength, and poor machining and fabrication characteristics. Also, being a cast material, the control of internal porosities and non-uniformities present production problems. Nonetheless, with proper quality control, and with good engineering design and practices, these problems can be controlled. From a corrosion standpoint, tests of up to 524 h on Durichlor-51<sup>28</sup> have shown only a moderate amount of attack (5 μm surface penetration), but very importantly, corrosion appears to proceed very uniformly over the surface of this material. It therefore seems reasonable to extrapolate to a lifetime of the order of 5 y for this application. In contrast to Durichlor-51, another high silicon cast iron, Duriron, shows a rather irregular corrosion behavior with grain pullouts, corrosion pits and spallation in similar H<sub>2</sub>SO<sub>4</sub> corrosion tests at 673K.<sup>28</sup>

In view of the developments thus far, our choice of material for the H<sub>2</sub>SO<sub>4</sub> heat exchanger is siliconized SiC.

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